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(54) Title: STRUCTURED COMPOSITION COMPRISING A HETERATOME POLYMER AND FIBERS

(57) Abstract: The invention relates to a physiologically acceptable composition, in particular a cosmetic composition, containing at least one liquid fatty phase, at least one polymer for structuring the said fatty phase, having a weight-average molecular mass of less than 100 000 and in particular ranging from 1 000 to 30 000, comprising: a) a polymer skeleton having hydrocarbon-based repeating units containing at least one hereto atom, and optionally: b) pendent fatty chains and/or terminal fatty chains that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these units, and fibres, the liquid fatty phase, the structuring polymer and the fibre forming a physiologically acceptable medium. This composition is in particular in the form of a stick of lipstick or of foundation, is hard and stable, does not exude and its application gives a non-greasy deposit.

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# STRUCTURED COMPOSITION COMPRISING A HETEROATOME POLYMER AND FIBERS

The present invention relates to a care and/or treatment and/or make-up composition for the skin, including the scalp, and/or for the lips of human beings, containing a liquid fatty phase, structured with a polymer containing specific hetero atoms. This composition is stable over time and is especially in the form of a make-up stick and more especially a foundation or a lipstick, whose application produces a migration-resistant and non-greasy deposit.

The foundations currently marketed are usually either in the 10 form of a liquid packaged in a bottle, or in the form of a product compacted in a case (see in particular document US-A-5 186 318). These foundations require the use of an applicator such as a sponge, which rapidly becomes contaminated and must be cleaned very regularly, especially after each application. Thus, users of foundations are increasingly on the lookout for 15 solid forms in stick, in order to dispense with the sponge-type applicator. Such a foundation is easy to use, hygienic and can be applied until all of the product has been used up, unlike a conventional foundation applied with a sponge. Furthermore, the surface of the foundation remains smooth, whereas the surface of a product compacted in a case becomes deformed 20 under the pressure of the successive uptakes onto the applicator. Finally, it allows a uniform make-up effect to be obtained.

As regards conventional lipsticks and concealer products, these are usually in the form of a stick or rod. Deodorants and lipcare or antisun lip products are also produced in stick form.

These cosmetic or dermatological products contain a structured liquid fatty phase, i.e. a phase which is gelled and/or rigidified with structural agents such as waxes.

For the purposes of the invention, the expression "liquid fatty phase" means a fatty phase which is liquid at room temperature (25°C) and atmospheric pressure (760 mmHg), comprising one or more fatty

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substances that are liquid at room temperature, also referred to as oils, that are generally mutually compatible. The expression "liquid fatty substance" means a non-aqueous liquid medium which is immiscible in all proportions with water, and more especially a hydrocarbon-based compound comprising one or more carbon chains each containing at least 5 carbon atoms and possibly comprising polar groups such as a carboxylic acid, hydroxyl, polyol, amine, amide, phosphoric acid, phosphate, ester, ether, urea, carbamate, thiol, thioether or thioester group; a silicone compound optionally comprising carbon chains at the end or pendent, these chains optionally being substituted with a fluoro or perfluoro, (poly)amino acid, ether, hydroxyl, amine, acid or ester group; or a fluoro or perfluoro compound such as fluorohydrocarbons or perfluorohydrocarbons containing at least 5 carbon atoms, possibly comprising a hetero atom such as N, O, S or P and optionally one or more polar functions, such as an ether, ester, amine, acid, carbamate, urea, thiol or hydroxyl group. 15

For the purposes of the present invention, the term "wax" means a lipophilic fatty compound that is solid at room temperature (25°C) and atmospheric pressure (760 mmHg), which undergoes a reversible solid/liquid change of state, having a melting point of greater than 40°C and better still greater than 55°C and which may be up to 200°C, and having an anisotropic crystal organization in the solid state. The size of the crystals is such that the crystals diffract and/or scatter light, giving the composition a cloudy, more or less opaque appearance. By bringing the wax to its melting point, it is possible to make it miscible with oils and to form a microscopically homogeneous mixture, but on returning the temperature of the mixture to room temperature, recrystallization of the wax in the oils of the mixture is obtained, this recrystallization being responsible for the rigidification of the liquid fatty phase.

For the purposes of the invention, the waxes are those generally used in cosmetics and dermatology; they are especially of natural origin, for instance beeswax, carnauba wax, Candellila wax,

Ouricoury wax, Japan wax, paraffin wax, lignite wax, microcrystalline waxes, lanolin wax, montan wax, ozokerites and hydrogenated oils such as hydrogenated jojoba oil, as well as waxes of synthetic origin, for instance polyethylene waxes derived from the polymerization or copolymerization of ethylene, waxes obtained by Fischer-Tropsch synthesis, fatty acid esters and glycerides that are solid at 40°C and better still at above 55°C, silicone waxes such as alkyl- and alkoxy-poly(di)methylsiloxanes and/or poly(di)methylsiloxane esters that are solid at 40°C and better still at more than 55°C.

10 According to the invention, the melting point values correspond to the melting peak measured by the "Differential Scanning Calorimetry" method with a temperature rise of 5 or 10°C/min.

Unfortunately, the waxes currently used give the composition a greasy and oily feel and/or a greasy and lank sensation. Furthermore, manufacturing a stick with waxes often poses problems of reproducibility on 15 account of the melting point variability of the various waxes that are commercially available. In addition, the waxes have a tendency to make the composition matt, which is not always desirable, in particular for a lipstick or an eye shadow; specifically, women are always on the lookout for a lipstick in stick form which deposits a film that is comfortable, non-greasy and more and more glossy.

Now, the structuring of the liquid fatty phase with waxes makes it possible, in addition to obtaining a product in the form of a stick or tube, to limit the exudation (or syneresis) of the fatty phase from the solid compositions, especially in hot and humid regions, and to limit, after deposition on the skin or the lips, the migration of this phase in the wrinkles and fine lines, which is particularly desired for a lipstick, a concealer product or an eye shadow. Specifically, large migration of the liquid fatty phase, in particular when it is charged with dyestuffs, leads to an anaesthetic effect around the lips and the eyes, which particularly accentuates the wrinkles and fine lines. This migration is often mentioned

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by women as being a major defect of conventional lipsticks, concealer products and eye make-ups in stick form. The term "migration" means a running of the composition beyond the initial application line.

The structuring of the liquid fatty phase and the limitation of its exudation and of the migration of the deposit on the skin or the lips increase as the wax content increases. Thus, the wax content is a constraining factor on the comfort and lightness of make-up products in stick form.

Furthermore, make-up compositions must have good staying or long wearing over time and in particular of the colour. The poor staying power is characterized by a colour change (turning, fading) or a non-uniform change in the make-up effect over time, generally following an interaction with sebum and/or sweat secreted by the skin, and, for the lips, an interaction with saliva. Specifically, a composition which does not have good staying power over time obliges the user to reapply the make-up regularly. However, women nowadays wish to achieve a beauty enhancement of their face and body while spending as little time as possible in doing so.

To overcome these drawbacks, the Applicant has envisaged replacing all or some of the waxes with polymers for structuring the liquid fatty phase, in particular of the polyamide, polyurea or polyurethane type. Unfortunately, the sticks obtained have a greater or lesser tendency to exudate, in particular in a hot and humid environment, and/or to become brittle when applied to the lips or the skin. This embrittlement may be reflected by breakage of the stick, during its shear on application.

The need thus remains for a composition which does not have the above drawbacks, which especially has good mechanical and thermal stability over time, even in hot and humid countries, and which produces a deposit on the skin or the lips that shows good staying power over time and/or that does not migrate. Furthermore, this composition is

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easy to manufacture and gives the deposit a comfortable and non-greasy sensation, both during application and over time.

A subject of the invention is, precisely, a care and/or make-up and/or treatment composition for the skin and/or the lips of the face and/or for superficial body growths, which makes it possible to overcome the drawbacks mentioned above.

The Applicant has found, surprisingly, that the use of specific polymers combined with one or more fibres makes it possible to obtain a composition especially in rigid form as a stick, whose application to the skin or the lips produces a deposit which has noteworthy cosmetic properties. In particular, the deposit is supple, comfortable, light and "migration-resistant".

Moreover, the composition is stable over time, withstands shear during application and does not exude at room temperature or at higher temperature (40 to 47°C approximately); it is heat stable. In addition, it has a pleasant, fondant texture and is of course slippery on the skin or the lips without being greasy.

The expression "heat stable" means a composition which does not exude at room temperature for at least 2 months, or even up to 9 months, or at 37°C or at 47°C for one month.

The invention applies not only to make-up products for the lips, such as lipsticks, lip glosses and lip pencils, but also to care and/or treatment products for the skin, including the scalp, and for the lips, such as antisun products especially in stick form for facial skin or the lips, care products for the human face or body, make-up products for the skin, both of the human face and body, such as foundations optionally cast in stick or dish form, concealer products, eye shadows, face powders, transfer tattoos, body hygiene products such as deodorants especially in stick form, shampoos, conditioners and make-up products for the eyes such as eyeliners, eye pencils and mascaras more especially in cake form, as well as make-up and care products for superficial body growths, for instance keratin fibres such as the hair, the eyelashes and the eyebrows.

More specifically, a subject of the invention is a composition containing at least one liquid fatty phase structured with at least one structuring polymer with a weight-average molecular mass of less than 1 000 000, comprising a) a polymer skeleton having hydrocarbon-based repeating units containing at least one hetero atom, and optionally b) at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms especially from 8 to 120 and being linked to these hydrocarbon-based units, and at least one or more fibres, the liquid fatty phase, the structuring polymer and the fibre forming a physiologically acceptable medium.

More especially, the weight-average molecular mass is less than 500 000 and better still less than 100 000.

The composition of the invention is in particular structured and can be in the form of a paste, a solid or a more or less viscous cream. It can be a simple or multiple emulsion such as an oil-in-water or water-in-oil emulsion or oil-in-water-in-oil or water-in-oil-in-oil emulsion, or a rigid or soft gel containing an oily continuous phase. More especially, the composition comprises a liquid fatty phase forming the continuous phase. In particular, it is in a form cast as a stick or a dish and more especially in the form of an oily rigid gel, in particular an anhydrous gel and especially an anhydrous stick. More especially, it is in the form of an opaque, translucent or transparent rigid gel (depending on the nature of the fibre and the presence of absence of pigments), the liquid fatty phase forming the continuous phase.

The structuring of the liquid fatty phase can be modified depending on the nature of the polymer containing a hetero atom and on the nature of the fibre that are used, and may be such that a rigid structure in the form of a rod or a stick is obtained. When these tubes are coloured, they make it possible, after application, to obtain a uniformly coloured deposit which does not migrate and which has good staying power, in particular of the colour over time.

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The composition of the invention is advantageously a composition for the skin or the lips and better still a foundation composition, concealer product, eye shadow or lipstick composition, in particular in stick form. The presence of fibres makes it possible to obtain a stick12.7 mm in diameter, corresponding to that usually used in lipsticks, which is hard and which does not break during repeated application to the skin or the lips.

The structuring polymer in the composition of the invention is a solid that is undeformable at room temperature (25°C) and atmospheric pressure (760 mmHg). It is capable of structuring the composition without opacifying it.

For the purposes of the invention, the expression "functionalized chain" means an alkyl chain comprising one or more functional or reactive groups chosen in particular from amide, hydroxyl, ether, oxyalkylene, polyoxyalkylene and halogen groups, including fluoro or perfluoro groups, ester, siloxane and polysiloxane groups. In addition, the hydrogen atoms of one or more fatty chains may be substituted at least partially with fluorine atoms.

According to the invention, these chains may be linked directly to the polymer skeleton or via an ester function or a perfluoro group.

For the purposes of the invention, the term "polymer" means a compound containing at least 2 repeating units and preferably at least 3 repeating units, which are identical.

According to the invention, the expression "hydrocarbonbased repeating units" means a unit containing from 2 to 80 carbon atoms
and preferably from 2 to 60 carbon atoms, bearing hydrogen atoms and
optionally oxygen atoms, which may be linear, branched or cyclic, and
saturated or unsaturated. These units each also comprise one or more
hetero atoms that are advantageously non-pendent but are in the polymer
skeleton. These hetero atoms are chosen from nitrogen, sulphur and
phosphorus atoms and combinations thereof, optionally combined with one

or more oxygen atoms. The units preferably comprise at least one nitrogen atom, in particular a non-pendent nitrogen atom. These units also advantageously comprise a carbonyl group.

The units containing a hetero atom are, in particular, amide

units forming a skeleton of the polyamide type, carbamate and/or urea
units forming a polyurethane, polyurea and/or polyurea-urethane skeleton.

These units are preferably amide units. The pendent chains are
advantageously linked directly to at least one of the hetero atoms of the
polymer skeleton. In one embodiment, the structuring polymer comprises a
polyamide skeleton.

Between the hydrocarbon-based units, the polymer may comprise silicone units or oxyalkylene units.

In addition, the polymer in the composition of the invention advantageously comprises a number of fatty chains which represents from 40% to 98% of the total number of units containing a hetero atom and of fatty chains, and better still from 50% to 95%. The nature and proportion of the units containing a hetero atom depends on the nature of the liquid fatty phase and is, in particular, similar to the nature of the fatty phase. Thus, the more the units containing a hetero atom are polar and in high proportion in the polymer, which corresponds to the presence of several hetero atoms, the greater the affinity of the polymer for polar oils. Conversely, the more non-polar, or even apolar, the units containing a hetero atom, or the lower the proportion thereof, the greater the affinity of the polymer for apolar oils.

A subject of the invention is also a composition containing at least one liquid fatty phase structured with at least one structuring polyamide having a weight-average molecular mass of less than 100 000, comprising a) a polymer skeleton containing amide repeating units and b) optionally at least one pendent fatty chain and/or at least one terminal chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these amide units, and at least one fibre, this

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liquid fatty phase, the fibre and the structuring polyamide forming a physiologically acceptable medium.

The pendent fatty chains are preferably linked to at least one of the nitrogen atoms in the amide units of the structuring polymer.

In particular, the fatty chains of this polyamide represent from 40% to 98% relative to the total number of amide units and of fatty chains, and better still from 50% to 95%.

The structuring polymer(s) and in particular the structuring polyamides in the composition according to the invention advantageously have a weight-average molecular mass of less than 50 000 and in particular ranging from 1 000 to 30 000, preferably from 2 000 to 20 000 and, for example, from 2 000 to 10 000.

As preferred structuring polymers which may be used in the invention, mention may be made of polyamides branched with pendent fatty chains and/or terminal fatty chains containing from 6 to 120 carbon 15 atoms and better still from 8 to 120 and in particular from 12 to 68 carbon atoms, each terminal fatty chain being linked to the polyamide skeleton via at least one link group, in particular an ester. These polymers preferably comprise a fatty chain at each end of the polymer skeleton and in particular of the polyamide skeleton. Other link groups which may be mentioned are ether, amine, urea, urethane, thioester, thiourea and thiourethane groups or a single bond.

These polymers are preferably polymers resulting from a polycondensation between a dicarboxylic acid containing at least 32 carbon atoms (in particular containing from 32 to 44 carbon atoms) and a diamine containing at least 2 carbon atoms (in particular from 2 to 36 carbon atoms). The diacid is preferably a dimer of a fatty acid containing at least 16 carbon atoms, for instance oleic acid, linoleic acid or linolenic acid. The diamine is preferably ethylenediamine, hexylenediamine or

hexamethylenediamine. For the polymers comprising one or 2 terminal 30 carboxylic acid groups, it is advantageous to esterify them with a

monoalcohol containing at least 4 carbon atoms, preferably from 10 to 36 carbon atoms, better still from 12 to 24 and even better from 16 to 24, for example 18 carbon atoms.

These polymers are more especially those disclosed in document US-A-5 783 657 from the company Union Camp. Each of these polymers in particular satisfies formula (I) below:

in which n denotes a number of amide units such that the number of ester groups represents from 10% to 50% of the total number of ester and amide groups; R¹ is, independently in each case, an alkyl or alkenyl group containing at least 4 carbon atoms and in particular from 4 to 24 carbon atoms; R² represents, independently in each case, a C₄ to C₄₂ hydrocarbon-based group, on condition that 50% of the groups R² represent a C₃₀ to C₄₂ hydrocarbon-based group; R³ represents, independently in each case, an organic group containing at least 2 carbon atoms, hydrogen atoms and optionally one or more oxygen or nitrogen atoms; and R⁴ represents, independently in each case, a hydrogen atom, a C₁ to C₁₀ alkyl group or a direct bond to R³ or to another R⁴, such that the nitrogen atom to which R³ and R⁴ are both attached forms part of a heterocyclic structure defined by R⁴-N-R³, with at least 50% of the groups R⁴ representing a hydrogen atom.

In the particular case of formula (I), the terminal fatty chains that are optionally functionalized for the purposes of the invention are terminal chains linked to the last hetero atom, in this case nitrogen, of the polyamide skeleton.

In particular, the ester groups of formula (I), which form part

of the terminal and/or pendent fatty chains for the purposes of the invention, represent from 15% to 40% of the total number of ester and amide groups and better still from 20% to 35%. Furthermore, n is advantageously an integer ranging from 1 to 5 and better still greater than 2, i.e. from 3 to 5. Preferably, R¹ is a C₁₂ to C₂₂ and preferably C₁₆ to C₂₂ alkyl group. Advantageously, R² can be a C₁₀ to C₄₂ hydrocarbon-based (alkylene) group. Preferably, at least 50% and better still at least 75% of the groups R² are groups containing from 30 to 42 carbon atoms. The other groups R³ are C₄ to C₁₆ and better still C₄ to C₁₂ hydrogen-containing groups. Preferably, R³ represents a C₂ to C₃₆ hydrocarbon-based group or a polyoxyalkylene group and R¹ represents a hydrogen atom. Preferably, R³ represents a C₂ to C₁₂ hydrocarbon-based group.

The hydrocarbon-based groups may be linear, cyclic or branched, and saturated or unsaturated groups. Moreover, the alkyl and alkylene groups may be linear or branched, and saturated or unsaturated groups.

According to the invention, the structuring of the liquid fatty phase is obtained with the aid of one or more polymers of formula (I). In general, the polymers of formula (I) are in the form of mixtures of polymers, these mixtures also possibly containing a synthetic product corresponding to a compound of formula (I) in which n is 0, i.e. a diester.

As examples of structuring polymers, which can be used in the composition according to the invention, mention may be made of the commercial products sold by the company Arizona Chemical under the names Uniclear 80 and Uniclear 100. They are sold, respectively, in the form of an 80% (in terms of active material) gel in a mineral oil and a 100% (in terms of active material) gel. They have a softening point of from 88 to 94°C. These commercial products are a mixture of copolymers of a C<sub>36</sub> diacid condensed with ethylenediamine, having a weight-average molecular mass of about 6 000. The terminal ester groups result from the esterification of the remaining acid endings with cetyl alcohol, stearyl

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alcohol or mixtures thereof (also known as cetylstearyl alcohol).

As structuring polymers which can be used in the invention, mention may also be made of polyamide resins resulting from the condensation of an aliphatic dicarboxylic acid and a diamine (including compounds containing more than 2 carbonyl groups and 2 amine groups), the carbonyl and amine groups of adjacent individual units being condensed via an amide bond. These polyamide resins are, in particular, those sold under the brand name Versamid® by the companies General Mills Inc. and Henkel Corp. (Versamid 930, 744 or 1655) or by the company Olin Mathieson Chemical Corp. under the brand name Onamid®, in particular Onamid S or C. These resins have a weight-average molecular mass ranging from 6 000 to 9 000. For further information regarding these polyamides, reference may be made to the documents US-A-3 645 705 and US-A-3 148 125. More especially, Versamid® 930 or 744 is used.

The polyamides sold by the company Arizona Chemical under the references Uni-Rez (2658, 2931, 2970, 2621, 2613, 2624, 2665, 1554, 2623 and 2662) and the product sold under the reference Macromelt 6212 by the company Henkel may also be used. For further information regarding these polyamides, reference may be made to document US-A-5 500 209.

It is also possible to use polyamide resins issued from vegetable sources, in particular such as those disclosed in the patents US-A-5783657 and US-A-5998570, the disclosures of which are herein incorporated by reference.

The structuring polymers in the composition of the invention advantageously have a softening point of greater than 65°C, which may be up to 190°C. They preferably have a softening point ranging from 70 to 130°C and better still from 80 to 105°C. This softening point is lower than that of the known structuring polymers, thus facilitating the use of the polymers that are the subject of the invention and limiting the degradation of the liquid fatty phase. These polymers are, in particular, non-waxy

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polymers.

The structuring polymers in the composition according to the invention preferably correspond to formula (I). On account of their fatty chain(s), these polymers are readily soluble in oils and thus lead to compositions that are macroscopically homogeneous even with a high content (at least 25%) of polymer, unlike polymers not containing a fatty chain.

According to the invention, the composition contains one or more fibres. The term "fibre" means any particle that is solid at room temperature and atmospheric pressure, whose length is greater than its apparent density, used alone or in combination, and which are insoluble in these ingredients, even when these ingredients are raised to a temperature above room temperature and in particular to their softening point or their melting point. These fibres are advantageously chemically inert, i.e. they do not react chemically with the various ingredients of the composition.

These fibres have melting points that are at least greater than 170°C and better still greater than 200°C. They may be absorbent or non-absorbent, i.e. capable in particular of absorbing the oils of the composition and also the biological substances secreted by the skin.

The fibres which can be used in the composition of the 20 invention may be fibres of synthetic or natural, and inorganic or organic origin. They may be short or long, flat, cylindrical or lamellar, individual or organized, for example in bundles, and hollow or solid. They can have any shape, and in particular a circular, elliptic or polygonal (triangular, square, hexagonal or octagonal) cross section depending on the specific application envisaged. In particular they can have blunt and/or rounded ends to prevent injury.

Their ends may also be multilobal and especially trilobal, pointed or rounded.

30 In particular, the fibres have a length ranging from 1 nm to 20 mm, preferably from 10 nm to 5 mm and better still from 0.1 mm to

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1.6 mm. Their cross section can be within a circle of diameter ranging from 2 nm to 150  $\mu$ m, preferably ranging from 20 nm to 120  $\mu$ m and better still from 500 nm to 80  $\mu$ m. The weight or yarn count of the fibres is often given in denier or decitex and represents the weight in grams per 9 km of yarn.

The fibres in the composition according to the invention preferably have a yarn count chosen in the range from 0.15 to 30 denier and better still from 0.18 to 18 denier.

Advantageously, the fibres have a length L and a diameter D such that L/D is chosen in the range from 1.5 to 2 500, preferably from 3.5 to 500 and better still from 5 to 150.

In order to obtain a glossy make-up, which is most particularly desired for making up the nails and the lips, short fibres in particular having a length ranging from 1 nm to 200  $\mu$ m are advantageously used.

Conversely, for a matt make-up, which is especially desired for making up the face (in particular for a powder or a foundation), long fibres especially having a length of greater than 200 µm are preferably used.

The fibres can be those used in the manufacture of textiles, and in particular silk, cotton, wool or flax fibres, cellulose fibres extracted in particular from wood, plants or algae, polyamide (Nylon®), cork, sugar can, rayon or viscose fibres, acetate fibres, in particular rayon acetate or cellulose acetate fibres, poly-(p-phenylene terephthalamide) fibres, in particular Kevlar® fibres or aramid fibres, acrylic fibres, in particular polymethyl methacrylate (PMMA) or poly-2-hydroxyethyl methacrylate fibres, polyolefin fibres and in particular polyethylene or polypropylene fibres, glass, silica or carbon fibres, in particular in graphite form, polytetrafluoroethylene (Teflon®), insoluble collagen, polyester, polyvinyl chloride or polyvinylidene chloride, polyvinyl alcohol, polyacrylonitrile, chitosan, polyurethane or polyethylene phthalate fibres, fibres formed from a mixture of polymers such as those mentioned above, for instance

polyamide/polyester fibres, and mixtures of these fibres.

It is also possible to use surgical fibres, such as resorbable

synthetic fibres prepared from glycolic acid and from caprolactone ("Monocryl" from Johnson & Johnson), resorbable synthetic fibres such as the copolymer of lactic acid and of glycolic acid ("Vicryl" from Johnson & Johnson), terephthalic polyester fibres ("Ethibond" from Johnson & Johnson) and stainless steel threads ("Steel" from Johnson & Johnson) in particular for use as nail varnishes.

Moreover, the fibres may or may not be surface-treated and may or may not be coated, in particular with a view to making them hydrophobic. As coated fibres which can be used in the invention, mention may be made of polyamide fibres coated with copper sulphide for an antistatic effect (for example the R-STAT fibres from Rhodia) or another polymer allowing a particular organization of the fibres (specific surface treatment) or a surface treatment which induces colour/hologram effects ("Lurex" fibre from Sildorex, for example).

Flat multilayer fibres having goniochromatic properties may also be used. Such fibres are disclosed in particular in the document EP-A-921217. They are formed from alternating layers of polyamide and polyester, in particular polyester terephthalate.

Fibres of synthetic origin and in particular organic fibres such as those used in surgery are preferably used.

In order to minimize the exudation of the composition in cast form, it is preferable for the fibre or mixture of fibres used in the composition to contain a chemical group of the same chemical nature as those of the units of the structuring polymer or a chemical group capable of forming physical bonds of the same type as that of the units of the polymer (self-complementary hydrogen bonds,  $\pi$  interactions between unsaturated rings or charge-transfer interactions, dipolar interactions, coordination bonds with organometallic derivatives). Thus, for structuring polymers containing units of the amide, urea and/or urethane type, the fibres used advantageously contain groups capable of forming hydrogen bonds, like these structuring polymers. As fibres capable of forming hydrogen bonds,

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mention may be made of fibres of acrylic polymer such as PMMA or poly(2-hydroxyethyl methacrylate), of poly-(p-phenylene terephthalamide), polyamide (Nylon®) fibres, polyurethane fibres and mixtures thereof. For units of the ester type, the fibres used may be of the polyester type.

The fibres which can be used in the composition according to the invention are preferably polyamide or poly-(p-phenylene terephthalamide) fibres. Their length (L) can range from 0.1 to 5 mm, preferably from 0.25 to 1.6 mm, and their average diameter (D) can range from 5 to 50  $\mu$ m. In particular, the polyamide fibres sold by Etablissements P. Bonte under the name Polyamide 0.9 Dtex 3 mm, having an average diameter from 15 to 20  $\mu$ m, a weight of about (0.9 Dtex) and a length ranging from 0.3 mm to 1.5 mm, can be used. Poly-p-phenylene terephthamide fibres with an average diameter of 12  $\mu$ m and a length of about 1.5 mm can also be used, such as those sold under the name Kevlar Floc by the company Du Pont Fibres.

The fibre concentration depends on the specific application and on the type of product envisaged. For a make-up product for the face such as a foundation or for the lips (such as a lipstick), the fibre concentration may range from 0.5% to 30% relative to the total weight of the composition, preferably from 2% to 20%. For a special effect, in particular as a make-up for the body, the nails or the hair, the amount of fibres can be up to 40% relative to the total weight of the composition. Then, according to the specific application, the fibre concentration may be ranged from 0.1 to 40%.

The polymer is also advantageously combined with at least one amphiphilic compound that is liquid and non-volatile at room temperature, having a hydrophilic/lipophilic balance (HLB) of less than 12 and in particular ranging from 1 to 8 and preferably from 1 to 5. According to the invention, one or more amphiphilic compounds may be used. The aim of these amphiphilic compounds is to reinforce the structuring properties of the polymer containing a hetero atom, to facilitate the use of

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the polymer and to improve the ability of the stick to be deposited.

According to the invention, the composition in stick form can have a hardness ranging from 30 to 300 g, preferably from 30 to 250 g and, for example, from 30 to 180 g.

The hardness of the composition can be measured by the so-called cheese-wire methods, which consists in cutting a stick of lipstick 8.1 mm in diameter and in measuring the hardness at 20°C using a DFGHS 2 tensile testing machine from Indelco-Chatillon, travelling at a speed of 100 mm/minute. It is expressed as the shear force (expressed in grams) required to cut a stick under these conditions.

The hardness of the composition according to the invention is such that the composition is advantageously self-supporting and can disintegrate easily to form a satisfactory deposit on the skin and/or the lips and/or superficial body growths. In addition, with this hardness, the composition of the invention has good impact strength. In addition, the hardness of the composition in stick form, together with its shear strength, increases as the amount of fibre increases.

According to the invention, the composition in stick form has the behaviour of a deformable, flexible elastic solid, giving noteworthy
20 elastic softness on application. The compositions in stick form of the prior art do not have this property of elasticity and flexibility.

The amphiphilic compound(s) which can be used in the composition of the invention comprise a lipophilic part linked to a polar part, the lipophilic part comprising a carbon-based chain containing at least 8 carbon atoms, in particular from 18 to 32 carbon atoms and better still from 18 to 28 carbon atoms. The polar part of this or these amphiphilic compound(s) is preferably the residue of a compound chosen from alcohols and polyols containing from 1 to 12 hydroxyl groups, and polyoxyalkylenes comprising at least 2 oxyalkylene units and containing from 0 to 20 oxypropylene units and/or from 0 to 20 oxyethylene units. In particular, the amphiphilic compound is an ester chosen from the hydroxystearates,

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oleates and isostearates of glycerol, of sorbitan or of methylglucose, or alternatively branched  $C_{12}$  to  $C_{26}$  fatty alcohols such as octyldodecanol, and mixtures thereof. Among these esters, monoesters and mixtures of monoand diesters are preferred.

The respective contents of fibre and of polymer containing a hetero atom and optionally that of the amphiphilic compounds are chosen according to the desired hardness of the composition and as a function of the specific application envisaged. The respective amounts of polymer, of fibre and optionally of amphiphilic compound should be such that they produce a stick, which can be worn down. In practice, the amount of polymer represents from 0.5% to 80% of the total weight of the composition, preferably from 2% to 60% and better still from 5% to 40%. The fibre content can advantageously represent from 0.1% to 40% relative to the total weight of the composition, preferably from 1% to 30% and better still from 5% to 20%. The amount of amphiphilic compound in practice represents from 0.1% to 35% of the total weight of the composition, for example from 1% to 20% and better still from 1% to 15%, if it is present.

The liquid fatty phase of the composition advantageously

contains more than 30% and better still more than 40% of liquid oil(s)

having a chemical nature close to the one of the skeleton of the structurant
polymer, and for example from 50% to 100%. In particular, the liquid fatty
phase structured with a polyamide-type skeleton contains a high quantity,
i.e. greater than 30% and better still greater than 40% relative to the total

weight of the liquid fatty phase and for example from 50% to 100%, of
apolar and more especially hydrocarbon-based oil or mixture of oils. For
the purposes of the invention, the expression "hydrocarbon-based oil"
means an oil essentially comprising carbon and hydrogen atoms, optionally
with one or more hydroxyl, ester or ether groups.

For a liquid fatty phase structured with a polymer containing a partially silicone-based skeleton, this fatty phase preferably contains more

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than 30% and better still more than 40% by weight, relative to the total weight of the liquid fatty phase and, for example, from 50% to 100%, of silicone-based liquid oil or mixture of oils, relative to the total weight of the liquid fatty phase.

For a liquid fatty phase structured with an apolar polymer of the hydrocarbon-based type, this fatty phase advantageously contains more than 30% and better still more than 40% by weight, and for example from 50% to 100%, of liquid apolar and in particular hydrocarbon-based oil or mixture of oils, relative to the total weight of the liquid fatty phase.

In particular, the polar oils of the invention are:

- hydrocarbon-based plant oils with a high content of triglycerides consisting of fatty acid esters of glycerol in which the fatty acids may have varied chain lengths from C<sub>4</sub> to C<sub>24</sub>, these chains possibly being linear or branched, and saturated or unsaturated; these oils are, in particular, wheat germ oil, corn oil, sunflower oil, karite butter, castor oil, sweet almond oil, macadamia oil, apricot oil, soybean oil, cotton oil, alfalfa oil, poppy oil, pumpkin oil, sesame oil, marrow oil, rape seed oil, avocado oil, hazelnut oil, grape seed oil, blackcurrant seed oil, evening primrose oil, millet oil, barley oil, quinoa oil, olive oil, rye oil, safflower oil, candlenut oil, passion flower oil and musk rose oil; or alternatively caprylic/capric acid triglycerides such as those sold by Stearineries Dubois or those sold under the names Miglyol 810, 812 and 818 by Dynamit Nobel;
- synthetic oils or esters of formula R<sub>5</sub>COOR<sub>6</sub> in which R<sub>5</sub> represents a linear or branched fatty acid residue containing from 1 to 40 carbon atoms and R<sub>6</sub> represents an in particular branched hydrocarbon-based chain containing from 1 to 40 carbon atoms, on condition that R<sub>5</sub> + R<sub>6</sub> 10, such as, for example, purcellin oil (cetostearyl octanoate), isononyl isononanoate, C<sub>12</sub>-C<sub>15</sub> alkyl benzoates, isopropyl myristate, 2-ethylhexyl palmitate, and alkyl or polyalkyl octanoates, decanoates or ricinoleates;
- 30 hydroxylated esters such as isostearyl lactate and diisostearyl malate; and pentaerythritol esters;

- synthetic ethers containing from 10 to 40 carbon atoms;
- $C_8$  to  $C_{26}$  fatty alcohols such as oleyl alcohol;
- C<sub>8</sub> to C<sub>26</sub> fatty acids such as oleic acid, linolenic acid or linoleic acid;
- mixtures thereof.

The apolar oils according to the invention are, in particular, 5 silicone oils such as volatile or non-volatile, linear or cyclic polydimethylsiloxanes (PDMSs) that are liquid at room temperature; polydimethylsiloxanes comprising alkyl or alkoxy groups which are pendent and/or at the end of the silicone chain, the groups each containing from 2 to 24 carbon atoms; phenylsilicones such as phenyl trimethicones, phenyl dimethicones, phenyl trimethylsiloxy diphenylsiloxanes, diphenyl dimethicones, diphenyl methyldiphenyl trisiloxanes and 2-phenylethyl trimethylsiloxysilicates; linear or branched, volatile or non-volatile hydrocarbons of synthetic or mineral origin, such as volatile liquid paraffins (such as isoparaffins and isododecane) or non-volatile liquid paraffins and 15 derivatives thereof, petroleum jelly, liquid lanolin, polydecenes, hydrogenated polyisobutenes such as parleam, and squalane; and mixtures thereof. The structured oils, and more especially those structured with polyamides and in particular those of formula (I) or the polyurethanes or polyureas or polyurea-urethanes, are preferably apolar oils and more 20 especially an oil or a mixture of oils of the hydrocarbon-based type of mineral or synthetic origin, chosen in particular from hydrocarbons, especially alkanes such as parleam oil, isoparaffins including isododecane, and squalane, and mixtures thereof. These oils are advantageously combined with one or more phenylsilicone oils. 25

The liquid fatty phase preferably contains at least one non-volatile oil chosen in particular from hydrocarbon-based oils of mineral, plant or synthetic origin, synthetic esters or ethers, silicone oils and mixtures thereof.

In practice, the total liquid fatty phase represents from 5% to 99% relative to the total weight of the composition, preferably from 10% to 80% and better still from 20% to 75%.

For the purposes of the invention, the expression "volatile solvent or oil" means any non-aqueous medium capable of evaporating on contact with the skin or the lips in less than one hour at room temperature and atmospheric pressure. The volatile solvent(s) of the invention is(are) organic solvents and in particular volatile cosmetic oils that are liquid at room temperature, having a non-zero vapour pressure, at room temperature and atmospheric pressure, ranging in particular from 10<sup>-2</sup> to 300 mmHg and preferably greater than 0.3 mmHg. The expression "non-volatile oil" means an oil, which remains on the skin or the lips at room temperature and atmospheric pressure for at least several hours and in particular having a vapour pressure of less than 10<sup>-2</sup> mmHg.

The liquid fatty phase advantageously contains at least one volatile solvent. Thus, a subject of the invention is also the use of a combination of at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, and of at least one fibre and of a volatile solvent in a physiologically acceptable composition, as an agent for limiting the transfer of the said composition and/or the deposition of marks on a support placed in contact with the said composition.

A subject of the invention is also a cosmetic process for limiting, or even preventing, the transfer of a cosmetic composition onto a support placed in contact with the said composition, which consists in manufacturing a composition containing at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less

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than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 8 to 120 carbon atoms and being linked to these hydrocarbon-based units, and in introducing fibres and at least one volatile solvent into the said composition.

According to the invention, these volatile solvents improve, in particular, the staying power or long wearing over time of the composition on the skin, the lips or superficial body growths. Also, the composition advantageously contains at least one volatile solvent, and better still a volatile oil. This solvent may be chosen from hydrocarbon-based solvents, silicone solvents optionally comprising alkyl or alkoxy groups that are pendent or at the end of a silicone chain, fluoro solvents and mixtures thereof.

As volatile solvents which can be used in the invention, mention may be made of linear or cyclic silicone oils having a viscosity at room temperature of less than 8 cSt and in particular containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. As volatile silicone oils which can be used in the invention, mention may be made in particular of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethylcyclohexasiloxane, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane and dodecamethylpentasiloxane and mixtures thereof.

As other volatile solvents which can be used in the invention, mention may be made of hydrocarbon-based volatile oils containing from 8 to 16 carbon atoms and mixtures thereof, and in particular branched  $C_8$ - $C_{16}$  alkanes such as  $C_8$ - $C_{16}$  isoalkanes (also known as isoparaffins) of petroleum origin, isodecane, isodecane, isohexadecane and, for example, the oils sold under the trade names Isopars or Permetyls,  $C_8$ - $C_{16}$  branched

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esters such as isohexyl neopentanoate, and mixtures thereof. The volatile solvent is preferably chosen from hydrocarbon-based volatile oils containing from 8 to 16 carbon atoms, and mixtures thereof.

Volatile fluoro solvents can also be used.

Isododecane (Permetyls 99 A) and  $C_8$ - $C_{16}$  isoparaffins (Isopars L.E.H) and mixtures thereof, optionally combined with decamethyltetrasiloxane, are preferably used.

The volatile solvent or the mixture of volatile solvents in particular represents a mass content of from 0% to 97.5% relative to the total weight of the composition, preferably from 1% to 75% and better still from 10% to 60%, for example from 20% to 60%. In general, the volatile solvent or the mixture of volatile solvents should be in an amount that is sufficient to obtain good staying power properties and should be adapted by a person skilled in the art as a function of the desired intensity for these staying power properties.

The composition of the invention can also comprise any additive usually used in the field under consideration, chosen in particular from antioxidants, essential oils, preserving agents, fragrances, waxes, fillers, products that are pasty at room temperature, neutralizing agents, liposoluble polymers or polymers that are dispersible in the medium, fatty-phase gelling agents, cosmetic or dermatological active agents such as, for example, emollients, moisturizers, vitamins, essential fatty acids, sunscreens, dispersants and mixtures thereof. These additives may be present in the composition in a proportion of from 0% to 20% (in particular from 0.01% to 20%) relative to the total weight of the composition and better still from 0.01% to 10% (if present).

The composition of the invention can also contain, as additive, an aqueous phase containing water that is optionally thickened or gelled with an aqueous-phase thickener or gelling agent and optionally water-miscible compounds. For a water-in-oil or oil-in-water emulsion, from 2% to 70% by weight of water and better still from 5% to 50% can be used.

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Needless to say, a person skilled in the art will take care to select the optional additional additives and/or the amount thereof such that the advantageous properties of the composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

The composition advantageously contains chemically inert spherical fillers, with a view to improving the disintegration of the composition in particular in solid form. The spherical fillers are those conventionally used in cosmetics and in particular polyamide (Nylon®) or PMMA fillers, and mixtures thereof.

The composition according to the invention can be in the form of a tinted dermatological composition or a care composition for keratin materials such as the skin, the lips and/or superficial body growths, in the form of an antisun composition or body hygiene composition in particular in the form of a deodorant product or make-up-removing product in stick form. It can be used in particular as a care base for the skin, superficial body growths or the lips (lip balms, for protecting the lips against cold and/or sunlight and/or the wind, or care cream for the skin, the nails or the hair).

The composition of the invention may also be in the form of a coloured make-up product for the skin, in particular a foundation, optionally having care or treating properties, a blusher, a face powder, an eye shadow, a concealer product, an eyeliner, a make-up product for the body; a make-up product for the lips such as a lipstick or a lip gloss, optionally having care or treating properties; a make-up product for superficial body growths such as the nails or the eyelashes, in particular in the form of a mascara cake, or for the eyebrows and the hair, in particular in the form of a pencii.

Needless to say, the composition of the invention should be cosmetically or dermatologically acceptable, i.e. it should contain a non-toxic physiologically acceptable medium and should be able to be applied to the skin, superficial body growths or the lips of human beings. For the

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purposes of the invention, the expression "cosmetically acceptable" means a composition of pleasant appearance, odour and feel.

The composition advantageously contains at least one cosmetic active agent and/or one dermatological active agent and/or at least one dyestuff.

The dyestuff according to the invention may be chosen from the liposoluble dyes, hydrophilic dyes, pigments and nacres usually used in cosmetic or dermatological compositions, and mixtures thereof. This dyestuff is generally present in a proportion of from 0.01% to 50% relative to the total weight of the composition, preferably from 0.5% to 40% and better still from 5% to 30%, if it is present. In the case of a composition in the form of a free or compacted powder, the amount of dyestuff in the form of solid particles that are insoluble in the medium (nacres and/or pigments) may be up to 90% relative to the total weight of the composition.

The liposoluble dyes are, for example, Sudan Red, D&C Red 17, D&C Green 6, β-carotene, soybean oil, Sudan Brown, D&C Yellow 11, D&C Violet 2, D&C Orange 5, quinoline yellow or annatto. They can represent from 0.1% to 20% of the weight of the composition and better still from 0.1% to 6% (if present). The water-soluble dyes are, for example, beetroot juice or methylene blue, and can represent up to 6% relative to the total weight of the composition.

The pigments may be white or coloured, mineral and/or organic, and coated or uncoated. Among the mineral pigments which may be mentioned are titanium dioxide, optionally surface-treated, zirconium oxide, zinc oxide or cerium oxide, as well as iron oxide or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue. Among the organic pigments which may be mentioned are carbon black, pigments of D & C type, and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium. The pigments can represent from 0.1% to 50%, preferably from 0.5% to 40% and better still from 2% to 30% relative to the total weight of the composition, if they are present.

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The nacreous pigments may be chosen from white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as titanium mica with iron oxides, titanium mica with, in particular, ferric blue or chromium oxide, titanium mica with an organic pigment of the type mentioned above, as well as nacreous pigments based on bismuth oxychloride. They can represent from 0.1% to 20% relative to the total weight of the composition, and better still from 0.1% to 15%, if they are present, and may or may not be surface-treated.

The composition can optionally contain one or more waxes to improve the structuring in stick form, although this rigid form can be obtained in the absence of wax. The composition advantageously contains little or no wax, and in particular less than 5% wax, when it is desired to obtain a translucent or transparent and/or glossy composition.

The composition of the invention also advantageously contains at least one polymer that is liposoluble or dispersible in the medium, in particular having an average molecular weight of from 500 to 1 000 000 and better still from 1 to 500 000, for example from 5 000 to 100 000 or better still from 5 000 to 20 000. This(these) liposoluble polymer(s) contribute in particular towards increasing the viscosity and/or improving the staying power of the film. These liposoluble polymers advantageously have a softening point of not more than 30°C.

As examples of liposoluble polymers which can be used in the invention, mention may be made of: polyalkylenes, in particular polybutene, poly(meth)acrylates, alkylcelluloses with a linear or branched, saturated or unsaturated  $C_1$  to  $C_6$  alkyl radical, such as ethylcellulose and propylcellulose, silicone polymers that are compatible with the fatty phase, as well as vinylpyrrolidone (VP) copolymers, and mixtures thereof.

The liposoluble or dispersible polymers in the composition of the invention are advantageously used in an amount of from 0% to 20% (as active material) relative to the total weight of the composition and better still

from 0.5% to 10%, if they are present.

The composition according to the invention also advantageously contains at least one fatty compound that is pasty at room temperature. For the purposes of the invention, the expression "pasty fatty compound" means fatty compounds with a melting point ranging from 20 to 55°C, preferably 25 to 45°C, and/or a viscosity at 40°C ranging from 0.1 to 40 Pa.s (1 to 400 poises), preferably 0.5 to 25 Pa.s, measured using a Contraves TV or Rhéomat 80 viscometer, equipped with a spindle rotating at 60 Hz. A person skilled in the art can select the spindle for measuring the viscosity from the spindles MS-r3 and MS-r4, on the basis of his general knowledge, so as to be able to carry out the measurement of the pasty compound tested.

According to the invention, one or more pasty fatty substances are used. These fatty substances are preferably hydrocarbon-based compounds, optionally of polymeric type; they can also be chosen from silicone compounds and/or fluoro compounds; they may also be in the form of a mixture of hydrocarbon-based compounds and/or silicone compounds and/or fluoro compounds. In the case of a mixture of different pasty fatty substances, the hydrocarbon-based pasty compounds (containing mainly hydrogen and carbon atoms and optionally ester groups) are preferably used in major proportion.

Among the pasty compounds which may be used in the composition according to the invention, mention may be made of lanolins and lanolin derivatives such as acetylated lanolins of oxypropylenated lanolins or isopropyl lanolate, having a viscosity of from 18 to 21 Pa.s, preferably 19 to 20.5 Pa.s, and/or a melting point of from 30 to 55°C, and mixtures thereof. It is also possible to use esters of fatty acids or of fatty alcohols, in particular those containing from 20 to 55 carbon atoms (melting point of about from 20 to 35°C and/or viscosity at 40°C ranging from 0.1 to 40 Pa.s), such as triisostearyl or cetyl citrate; arachidyl propionate; polyvinyl laurate; cholesterol esters, such as triglycerides of plant origin,

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such as hydrogenated plant oils, viscous polyesters such as poly(12-hydroxystearic acid), and mixtures thereof. Triglycerides of plant origin which may be used are hydrogenated castor oil derivatives, such as "Thixinr" from Rhéox.

Mention may also be made of pasty silicone fatty substances such as polydimethylsiloxanes (PDMSs) containing pendent chains of the alkyl or alkoxy type containing from 8 to 24 carbon atoms, and having a melting point of 20-55°C, such as stearyldimethicones, in particular those sold by Dow Corning under the trade names DC2503 and DC25514, and mixtures thereof.

The pasty fatty substance(s) may be present in a proportion of from 0% to 60% by weight, relative to the total weight of the composition, preferably in a proportion of from 0.5% to 45% by weight, and even more preferably in a proportion of 2-30% by weight, in the composition, if they are present.

The composition according to the invention may be manufactured by the known processes, that are generally used in cosmetics or dermatology. They may be manufactured by the process, which consists in heating the polymer at least to its softening point, in adding the amphiphilic compound(s), the dyestuffs and the additives thereto and then in mixing everything together until a clear, transparent solution is obtained. After reducing the temperature of the mixture obtained, the volatile solvent(s) is (are) then added. The homogeneous mixture obtained can then be cast in a suitable mould such as a lipstick mould or directly into the packaging articles (case or dish in particular).

Another subject of the invention is a make-up composition, in particular in stick form, containing at least one continuous liquid fatty phase structured with at least one non-waxy structuring polymer having a weight-average molecular mass of less than 100 000, and at least one or more fibres, the liquid fatty phase, the structuring polymer and the fibre forming a physiologically acceptable medium. In particular, the fibre and the

structuring polymer give the composition the appearance of a deformable elastic solid having a hardness ranging from 30 to 300 g, even in the absence of wax.

The non-waxy polymer is advantageously a polymer whose skeleton comprises hydrocarbon-based units containing a hetero atom, as defined above.

A subject of the invention is also a care, make-up or treatment composition for keratin materials of human beings, and in particular the skin, the lips and superficial body growths, comprising the application to the keratin materials of the composition, in particular the cosmetic composition, as defined above.

A subject of the invention is also the use of a combination of at least one polymer having a weight-average molecular mass of less than 100 000 and better still less than 50 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, and of at least one fibre, in a cosmetic composition or for the manufacture of a physiologically acceptable composition, which is solid, in particular without wax, which does not exude and/or which gives a migration-resistant and/or non-greasy deposit on keratin materials.

A subject of the invention is also the use of at least one fibre (one or more fibres) in a physiologically acceptable composition, containing at least one polymer having a weight-average molecular mass of less than 100 000 and better still less than 50 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based

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units, as an agent for increasing the hardness of the said composition and/or its shear strength and/or its heat resistance.

Another subject of the invention is a cosmetic process for increasing the hardness of a physiologically acceptable composition cast in particular as a stick or as a dish and/or for increasing its shear strength and/or its heat resistance, the said composition containing at least one polymer having a weight-average molecular mass of less than 100 000 and better still less than 50 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, which consists in introducing a sufficient amount of fibres into the said composition.

Another subject of the invention is an use of at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing 20 from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, in a physiologically acceptable composition comprising fibres, for improving the dispersion of said fibres in said composition.

Another subject of the invention is an use of at least one structuring polyamide having a weight-average molecular mass of less than 100 000, comprising a) a polymer skeleton containing amide repeating units and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these amide units, in a physiologically acceptable composition comprising fibres, for improving the dispersion of said fibres in said composition. The invention is illustrated in

greater detail in the examples, which follow. The amounts are given as percentages by mass.

### Example 1: Lipstick

Several lipsticks having a diameter of 12,7b mm and being different from each other in the amount X of fibres were prepared and their shear and their cosmetic properties where compared. X ranged from 0% to 10%. The composition was as follows:

| Uniclear 100  | 25%     |
|---|---------|
| • 2-octyldodecanol  | 10%     |
| <ul> <li>hydrogenated isoparaffin (Parleam)</li> </ul>    | qs 100% |
| <ul> <li>polyamide fibre (3 mm long, 0.9 Dtex)</li> </ul> | X%      |
| • pigments .  | 5%      |

#### **Procedure**

The fibres were predispersed in a Uniclear 100/isoparaffin

(Parleam) mixture using a spatula. The paste obtained was ground in a three-roll mill.

The Uniclear 100 + the 2-octyldodecanol + the Parleam + the pigments were mixed together with stirring (Raynerie turbomixer, at 1 000 rpm) at 100°C.

The fibre predispersion was finally added.

Stirring was continued (at 800 rpm) for 30 min. The preparation was cast in a lipstick mould. The product was placed at -20°C for 30 min and then removed from the mould.

Table I

| AMOUNT OF | SHEAR (g) TEXTURE                 |                   |  |
|-----------|-----------------------------------|-------------------|--|
| FIBRES    |                                   |                   |  |
| 0.5 g     | 90                                | release of oil    |  |
| Ì         | with breakage of the stick at the |                   |  |
| i         | base                              |                   |  |
| 1 g       | 96                                | no release of oil |  |
|           | no breakage of the stick          |                   |  |
| 5 g       | 130                               | no release of oil |  |
|           | no breakage of the stick          |                   |  |

## Conclusion:

From Table I, the higher the fibre concentration, and the higher the shear, irrespective of the storage temperature (RT, 4°C and 45°C). In addition, an improvement is found in the exudation stability (at 45°C) by incorporation of fibres. This improvement appears at and above 1% polyamide fibres.

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# Example 2: Anhydrous cast foundations

Several foundations differing from each other in the amount Y of fibre were prepared and their cosmetic properties were compared. Y ranged from 0% to 10%. The composition was as follows:

| Uniclear 100  | 25%     |
|---|---------|
| • isododecane   | 15%     |
| <ul> <li>polyamide fibre (3 mm long, 0.9 Dtex)</li> </ul> | Y%      |
| • pigments  | 8%      |
| hydrogenated isoparaffin                                  | qs 100% |

In the absence of fibre, the foundations exude oil at the surface, which gives a shiny greasy appearance and prevents uniform disintegration. At and above 1% fibre, the release of oil disappears and the uptake of product becomes uniform.

The cosmetic qualities of the product (appearance, disintegration, absence of release of oil) are conserved up to 5% fibre.

The procedure is the same as that of Example 1.

The compositions obtained have a pleasant, non-greasy, light, fondant feel under the fingers and are easy to spread.

Finally, these compositions were considered as applying well,

having a soft feel, being comfortable and producing a light make-up. The
skin is unified and the make-up effect is homogeneous. Furthermore, these
compositions have good staying power over time (no colour change and
gradual and uniform reduction over time of the make-up effect). The
presence of isododecane also makes it possible to improve their transferresistance properties.

# Example 3: Anhydrous foundation

| Uniclear 100  | 11% |
|---|-----|
| Parleam   | 10% |
| <ul> <li>polyamide fibre (0.3 mm long, 0.9 Dtex)</li> </ul> | 5%  |

| • pigments    | 10%     |
|---------------|---------|
| • isododecane | qs 100% |

These foundations are manufactured according to the procedure of Example 1.

# Example 4: Eye shadow

| Uniclear 100                            | 11%     |
|---|---------|
| Parleam                                 | 10%     |
| • polyamide fibre (3 mm long, 0.9 Dtex) | Z%      |
| Nylon-12 powder (spherical filler)      | Т%      |
| Blue 1 Al lake                          | 0.1%    |
| • isododecane                           | qs 100% |

The amount of fibres Y and the amount of Nylon-12 powder (spherical fillers) were varied. The results obtained are given in Table II.

Table II

| AMOUNT OF FILLERS | AMOUNT OF<br>FIBRES | TEXTURE  |
|-------------------|---------------------|--|
| T in g            | Zing                |  |
| 0                 | 0                   | Large transfer, release of oil.                                      |
| 0                 | 1                   | Slight transfer with sebum, satisfactory disintegration.             |
| 8                 | 2                   | Very slight transfer with sebum. Non-<br>greasy feel.                |
| . 5               | 5                   | Slight transfer, satisfactory disintegration. Pleasant feel.         |
| 0                 | 5                   | Slight transfer, surface of the stick smooth, slight disintegration. |
| 10                | 0                   | Difficult to disintegrate.   |

It emerges from Table II that the presence of fibres, optionally combined with fillers, improves the transfer-resistance property compared with a composition not containing any fibres.

Moreover, the combination of spherical fillers with fibres improves the disintegration of the product and thus makes it easier for the make-up to be deposited on the skin.

### CLAIMS

- structured with at least one structuring polymer with a weight-average molecular mass of less than 1 000 000, comprising a) a polymer skeleton having hydrocarbon-based repeating units containing at least one hetero atom, and optionally b) at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, and at least one or more fibres, the liquid fatty phase, the structuring polymer and the fibre forming a physiologically acceptable medium.
  - 2. Composition according to Claim 1, characterized in that the average molar mass is less than 500 000 and better still less than 100 000.
- 3. Composition according to Claim 1 or 2, characterized in that the units comprise a nitrogen atom.
  - Composition according to one of the preceding claims,
     characterized in that the units containing a hetero atom are amides.
  - 5. Composition according to one of the preceding claims, characterized in that the fatty chains represent from 40% to 98% and better still from 50% to 95% of the total number of units containing a hetero atom and of fatty chains.
  - 6. Composition according to one of the preceding claims, characterized in that the pendent fatty chains are linked directly to at least one of the said hetero atoms.
- 7. Structured composition containing at least one liquid fatty phase structured with at least one structuring polyamide having a weight-average molecular mass of less than 100 000, comprising a) a polymer skeleton containing amide repeating units and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these amide units, and one or more fibres, this liquid fatty phase,

the structuring polymer and the fibre(s) forming a physiologically acceptable medium.

- 8. Composition according to the preceding claim, characterized in that the fatty chains represent from 40% to 98% relative to the total number of amide units and of fatty chains.
- 9. Composition according to Claim 7 or 8, characterized in that the fatty chains represent from 50% to 95% relative to the total number of amide units and of fatty chains.
- 10. Composition according to one of Claims 7 to 9,

  characterized in that the pendent fatty chains are linked directly to at least one of the nitrogen atoms in the amide units.
  - 11. Composition according to one of the preceding claims, characterized in that the weight-average molar mass ranges from 1 000 to 30 000 and better still from 2 000 to 20 000 and even better still from 2 000 to 10 000.
  - 12. Composition according to one of the preceding claims, characterized in that the terminal fatty chain(s) is (are) linked to the skeleton via link groups.
- 13. Composition according to Claim 12, characterized in that the link groups are ester groups.
  - 14. Composition according to one of the preceding claims, characterized in that the fatty chain(s) contain(s) from 12 to 68 carbon atoms.
- 15. Composition according to one of the preceding claims, characterized in that the polymer is chosen from the polymers of formula (I) below, and mixtures thereof:

in which n denotes a number of amide units such that the number of ester groups represents from 10% to 50% of the total number of ester and amide groups; R¹ is, independently in each case, an alkyl or alkenyl group containing at least 4 carbon atoms; R² represents, independently in each case, a C₄ to C₄₂ hydrocarbon-based group, on condition that 50% of the groups R² represent a C₃₀ to C₄₂ hydrocarbon-based group; R³ represents, independently in each case, an organic group containing at least 2 carbon atoms, hydrogen atoms and optionally one or more oxygen or nitrogen atoms; and R⁴ represents, independently in each case, a hydrogen atom, a C₁ to C₁₀ alkyl group or a direct bond to R³ or another R⁴, such that the nitrogen atom to which R³ and R⁴ are both attached forms part of a heterocyclic structure defined by R⁴-N-R³, with at least 50% of the groups R⁴ representing a hydrogen atom.

- 16. Composition according to the preceding claim, characterized in that  $R^1$  is a  $C_{12}$  to  $C_{22}$  alkyl group.
- 17. Composition according to either of Claims 15 and 16, characterized in that R<sup>2</sup> are groups containing from 30 to 42 carbon atoms.
- 20 18. Composition according to one of the preceding claims, characterized in that the polymer represents from 0.5% to 80% relative to the total weight of the composition and better still from 5% to 40%.
  - 19. Composition according to one of the preceding claims, characterized in that the fibre(s) is (are) chosen from silk, cotton, wool or flax fibres, cellulose fibres extracted in particular from wood, plants or algae, polyamide, cork or sugar can, rayon or viscose fibres, acetate fibres, in particular rayon acetate, cellulose acetate or silk acetate fibres, poly-

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- (p-phenylene terephtalamide) fibres, acrylic fibres, in particular polymethyl methacrylate or poly-2-hydroxyethyl methacrylate fibres, polyolefin fibres and in particular polyethylene or polypropylene fibres, glass, silica or aramid fibres, carbon fibres, in particular in graphite form,
- polytetrafluoroethylene, insoluble collagen, polyester, polyvinyl chloride or polyvinylidene chloride, polyvinyl alcohol, polyacrylonitrile, chitosan, polyurethane or polyethylene phthalate fibres, fibres of mixtures of polymers, surgical fibres, and mixtures of these fibres.
- 20. Composition according to any one of the preceding claims, characterized in that the fibres are fibres of synthetic origin.
  - 21. Composition according to one of the preceding claims, characterized in that the fibre(s) has (have) a chemical group of the same chemical nature as that of the units of the structuring polymer or a group capable of forming physical bonds of the same type as that of the units of the polymer.
  - 22. Composition according to one of the preceding claims, characterized in that the fibre is hydrophobic-treated.
  - 23. Composition according to any one of the preceding claims, characterized in that the fibres are polyamide fibres or poly-
- 20 (p-phenyleneterephthamide) fibres.
  - 24. Composition according to any one of the preceding claims, characterized in that the fibres have a length L and a diameter D such that L/D is chosen in the range from 1.5 to 2 500, preferably from 3.5 to 500 and better still from 5 to 150.
- 25. Composition according to any one of the preceding claims, characterized in that the fibres have a length ranging from 1 nm to 20 mm, preferably from 10 nm to 5 mm and preferably from 0.1 mm to 1.6 mm.
- 26. Composition according to one of the preceding claims, 30 characterized in that the fibre represents a mass content of from 0.1% to 40% relative to the total weight of the composition, preferably from 0,5% to

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30% and better still from 2% to 20%.

- 27. Composition according to one of the preceding claims, characterized in that the liquid fatty phase also contains at least one non-volatile oil.
- 28. Composition according to one of the preceding claims, characterized in that the liquid fatty phase also contains at least one non-volatile oil chosen from hydrocarbon-based oils of mineral, plant or synthetic origin, synthetic esters or ethers and silicone oils, and mixtures thereof.
- 29. Composition according to one of the preceding claims, characterized in that the liquid fatty phase contains at least 30%, relative to the total weight of the liquid fatty phase, of apolar oil and, for example, from 50% to 100% relative to the total weight of the liquid fatty phase.
- 30. Composition according to one of the preceding claims, characterized in that the liquid fatty phase represents from 5% to 99% relative to the total weight of the composition, preferably from 10% to 80% and better still from 20% to 75%.
  - 31. Composition according to one of the preceding claims, characterized in that the liquid fatty phase also contains at least one volatile solvent.
  - 32. Composition according to Claim 31, characterized in that the solvent is an isoparaffin.
  - 33. Composition according to one of the preceding claims, characterized in that it constitutes a care and/or treatment and/or make-up composition for keratin materials.
  - 34. Composition according to one of the preceding claims, characterized in that it also contains at least one dyestuff.
- 35. Composition according to Claim 31, characterized in that the dyestuff is chosen from lipophilic dyes, hydrophilic dyes, pigments and nacres, and mixtures thereof.
  - 36. Composition according to Claim 31 or 32,

characterized in that the dyestuff is present in a proportion of from 0.01% to 50% relative to the total weight of the composition, preferably from 0.5% to 40% and better still from 5% to 30%.

- 37. Composition according to one of the preceding claims, characterized in that it contains at least one additive chosen from water, amphiphilic compounds with an HLB value of less than 12, antioxidants, essential oils, preserving agents, fragrances, waxes, fillers, fatty substances that are pasty at room temperature, neutralizing agents, polymers that are liposoluble or dispersible in the medium, cosmetic or dermatological active agents and dispersants, and mixtures thereof.
  - 38. Composition according to one of the preceding claims, characterized in that it contains, further, fillers having a shape different from the shape of the fibres.
- 39. Composition according to one of the preceding claims,
   characterized in that it is in the form of a rigid gel, and in particular in the form of an anhydrous stick.
  - 40. Composition according to one of the preceding claims, characterized in that it is in the form of a mascara, an eyeliner, a foundation, a lipstick, a blusher, a deodorant product, a make-up-removing product, a make-up product for the body, an eye shadow, a face powder, a concealer product, a shampoo, a conditioner, an antisun product or a care product for the face or the body.
  - 41. Composition according to one of the preceding claims, characterized in that it is in the form of a stick with a hardness ranging from 30 to 300 g.
    - 42. Make-up composition, in particular in the form of a stick containing at least one liquid continuous fatty phase, one or more fibres and at least one non-waxy polymer having a weight-average molecular mass of less than 100 000, structuring the said liquid fatty phase, the polymer, the liquid fatty phase and the fibre forming a physiologically acceptable medium, the fibre(s) and the polymer giving the composition the

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appearance of a deformable elastic solid with a hardness ranging from 30 to 300 g, in the absence of wax.

- 43. Cosmetic care, make-up or treatment process for the keratin materials of human beings, comprising the application to the keratin materials of a cosmetic composition in accordance with one of the preceding claims.
  - weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, and of at least one fibre, in a cosmetic composition or for the manufacture of a physiologically acceptable composition, which is solid, which does not exude and/or which gives a migration-resistant and/or non-greasy deposit on keratin materials.
- 45. Use of at least one fibre in a physiologically acceptable composition, containing at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, as an agent for increasing the hardness of the said composition and/or its shear strength and/or its heat resistance.
- 46. Use of a combination of at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that

are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, and of at least one fibre and of a volatile solvent in a physiologically acceptable composition, as an agent for limiting the transfer of the said composition and/or the deposition of marks on a support placed in contact with the said composition.

- 47. Use according to one of Claims 43 to 46, characterized in that the fibre(s) has (have) a chemical group of the same chemical nature as those of the units of the structuring polymer or a group capable of forming physical bonds of the same type as that of the polymer units.
- 10 48. Use according to one of Claims 43 to 467, characterized in that the polymer is a polyamide comprising terminal groups containing an ester group comprising a hydrocarbon-based chain containing from 10 to 42 carbon atoms.
- 49. Use according to one of Claims 43 to 48, characterized
   in that the fibre is chosen from polymer fibres, polyamide fibres or poly-(p-phenyleneterephthamide) fibres.
  - 50. Use according to one of Claims 43 to 49, characterized in that the composition is free of wax.
- 51. Use according to one of Claims 43 to 50, characterized in that the polymer has a weight-average molecular mass ranging from 1 000 to 30 000.
- 52. Cosmetic process for increasing the hardness of a physiologically acceptable composition cast in particular as a stick or as a dish and/or its shear strength and/or its heat resistance, the said composition containing at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 6 to 120 carbon atoms and being

linked to these hydrocarbon-based units, which consists in introducing a sufficient amount of fibre into the said composition.

- transfer of a cosmetic composition onto a support placed in contact with the said composition, which consists in manufacturing a composition containing at least one polymer having a weight-average molecular mass of less than 1 000 000 and better still less than 500 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and b) optionally at least one pendent fatty chain and/or at least one terminal fatty chain that are optionally functionalized, containing from 8 to 120 carbon atoms and being linked to these hydrocarbon-based units, and in introducing fibres and at least one volatile solvent into the said composition.
- 54. Use of at least one polymer having a weight-average
  molecular mass of less than 1 000 000 and better still less than 500 000,
  comprising a) a polymer skeleton containing hydrocarbon-based repeating
  units containing at least one hetero atom, and b) optionally at least one
  pendent fatty chain and/or at least one terminal fatty chain that are
  optionally functionalized, containing from 6 to 120 carbon atoms and being
  linked to these hydrocarbon-based units, in a physiologically acceptable
  composition comprising fibres, for improving the dispersion of said fibres in
  said composition.
- 55. Use of at least one structuring polyamide having a weightaverage molecular mass of less than 100 000, comprising a) a polymer
  skeleton containing amide repeating units and b) optionally at least one
  pendent fatty chain and/or at least one terminal fatty chain that are
  optionally functionalized, containing from 6 to 120 carbon atoms and being
  linked to these amide units, in a physiologically acceptable composition
  comprising fibres, for improving the dispersion of said fibres in said
  composition.

#### INTERNATIONAL SEARCH REPORT

PCT/IB 00/01984

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/48 A61K7/40

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## B. FIELDS SEARCHED

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